

ANTIMICROBIAL POWDER COATED METAL SHEET

Publication number: WO02087339

Publication date: 2002-11-07

Inventor: MYERS FREDERICK A (US); PRICE LEROY R (US)

Applicant: PROPERTIES INC AK (US); MYERS FREDERICK A (US); PRICE LEROY R (US)

Classification:

- **international:** A01N25/34; A01N59/16; C09D5/03; C09D5/14;
A01N25/34; A01N59/16; C09D5/03; C09D5/14; (IPC1-7): A01N59/16; A01N25/34; B05D7/14; C09D5/14

- **European:** A01N25/34; A01N59/16; C09D5/03F; C09D5/14

Application number: WO2002US13637 20020430

Priority number(s): US20010287613P 20010430

Cited documents:

- US6093407
- US5180585
- US5491202
- US5387473
- US5681890

more >>

[Report a data error here](#)

Abstract of WO02087339

The present invention relates to metallic sheets having an improved antimicrobial property and also related to a method of manufacturing such sheets. More particularly, it relates to the continuous coating on metallic sheets with a resin composition containing antimicrobial additives. The surface of the metallic article is addorded antimicrobial properties by coating a dispersion of fine particles made of an antimicrobial ingredient on the surface of the metallic sheet dispersed in a uniform layer and cured or dried to affix to the metallic surface. The inorganic anti-bacterial particles are metal component-supporting oxides, phosphates and zeolite powders. The inorganic anti-bacterial core particles have at least a primary surface coating of at least one metal or metal compound having antimicrobial properties. Conventional powder coating processes apply the coating, e.g., by electrostatic application. The metallic article generally includes sheet articles made of metals, for example, metallic sheets made of stainless steel, conventional steel and aluminum sheets or plate.

Data supplied from the **esp@cenet** database - Worldwide

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 November 2002 (07.11.2002)

PCT

(10) International Publication Number
WO 02/087339 A1

(51) International Patent Classification⁷: A01N 59/16,
25/34, C09D 5/14, B05D 7/14

(21) International Application Number: PCT/US02/13637

(22) International Filing Date: 30 April 2002 (30.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/287,613 30 April 2001 (30.04.2001) US

(71) Applicant (for all designated States except US): AK PROPERTIES, INC. [US/US]; 705 Curtis Street, Middletown, OH 45043 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): MYERS, Frederick, A. [—/US]; 1512 Cambridge Drive, Middletown, OH 45042 (US). PRICE, Leroy, R. [—/US]; 5319 Whispering Woods, West Chester, OH 45069 (US).

(74) Agents: ALBAINY-JENEI, Stephen, R. et al.; Frost Brown Todd LLC, 2200 PNC Center, 205 East Fifth Street, Cincinnati, OH 45202 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/087339 A1

(54) Title: ANTIMICROBIAL POWDER COATED METAL SHEET

(57) Abstract: The present invention relates to metallic sheets having an improved antimicrobial property and also related to a method of manufacturing such sheets. More particularly, it relates to the continuous coating on metallic sheets with a resin composition containing antimicrobial additives. The surface of the metallic article is addorded antimicrobial properties by coating a dispersion of fine particles made of an antimicrobial ingredient on the surface of the metallic sheet dispersed in a uniform layer and cured or dried to affix to the metallic surface. The inorganic anti-bacterial particles are metal component-supporting oxides, phosphates and zeolite powders. The inorganic anti-bacterial core particles have at least a primary surface coating of at least one metal or metal compound having antimicrobial properties. Conventional powder coating processes apply the coating, e.g., by electrostatic application. The metallic article generally includes sheet articles made of metals, for example, metallic sheets made of stainless steel, conventional steel and aluminum sheets or plate.

- 1 -

ANTIMICROBIAL POWDER COATED METAL SHEET

Frederick A. Myers
LeRoy R. Price

Cross Reference to Related Applications

- [0001] This application claims priority under 35 U.S.C. 119 to United States provisional application Ser. No. 60/287,613, filed April 30, 2001, and entitled "Antimicrobial Powder Coated Metal Sheet" the disclosure of which is hereby expressly incorporated herein by reference.

Field of the Invention

- [0002] The present invention relates to metallic sheets having an improved antimicrobial property and also related to a method of manufacturing such sheets. More particularly, it relates to continuous methods of powder coating metallic sheets with a resin composition containing antimicrobial additives.

Background of the Invention

- [0003] Recently there has been a trend to develop materials possessing an antimicrobial property generally utilizing a metal, *e.g.*, silver, copper, zinc, *etc.* Metallic articles, especially stainless steel sheets, are known for their hygienic cleanliness. For example, with stainless steel, it is known to add antibacterial properties using metallic layers or alloy layers of chromium, titanium, nickel or iron containing silver, copper and/or zinc formed on their surface by sputtering or incorporating silver in the stainless steel and dispersing silver phases. In addition, it has been known for a long time that silver ions or copper ions or zinc ions have an antibacterial property. For example, a silver ion has

- 2 -

widely been used as a disinfectant in the form of silver nitrate. However, the use of silver nitrate as a solution is inconvenient for handling and would have limited durability.

- [0004] Generally, the incorporation of silver into a metal object or article itself has the disadvantage that the metal's characteristics are altered by the inclusion of the silver as well as the disadvantage of the high cost of the metals themselves. Such a metallic sheet or plate having the antibacterial ingredient deeply imbedded inside the sheet or plate does not exert any effective action upon bacteria attached to the surface making incorporation throughout the entire article uneconomical.
- [0005] Known thermoset resin compositions have been broadly used as coating material for various metals such as iron, aluminum, copper, and stainless steel since the compositions afford a coating which is superior in luster, transparency, hardness, weather resistance, chemical resistance and other properties. However, the coating, itself would have no antibacterial action in and of itself and such coatings often have insufficient adhesion to metals making it impossible to endure a forming process such as bending. As is apparent from the foregoing, an object of the present invention is to provide an antibacterial resin composition for coating of metals which withstands bending or forming processes and is usable for coated metal sheets.

Summary of the Invention

- [0006] The present invention provides a polymer composition containing oxide or zeolite particles and having an antibacterial property along with processes for coating the surface of metal sheets with such composition. Specifically, the present invention provides for a metal sheet coated with a polymer resin containing inorganic particles with antibacterial properties and the process for making such coated sheets.

- 3 -

- [0007] The inorganic anti-bacterial particles are metal component-supporting oxides and zeolite powders that are made from core particles selected from the group consisting of oxides of titanium, aluminum, zinc and copper, sulfates of calcium, strontium and barium, zinc sulfide, copper sulfide, zeolites, mica, talc, kaolin, mullite, zirconium phosphate and silica.
- [0008] Preferably, the particles are at least one zeolite at least part of which retains at least one metal ion having a bactericidal property at the ionic exchange sites of the zeolite particles.
- [0009] The inorganic anti-bacterial core particles have at least a primary surface coating or constituent, comprising of from about 0.05 to about 20% by weight based on the core particles, of at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures thereof. Preferably, the coating or constituent is at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, or mixtures thereof and mixtures thereof.
- [0010] According to one embodiment of the present invention, there is provided a metallic sheet having an antibacterial property characterized in that the sheet is coated with a polymer composed of at least one polymer in which is dispersed at least one zeolite at least part of which retains at least one metal ion having a bactericidal property at the ionic exchange sites of the zeolite particles and methods for producing such metal sheets.
- [0011] The process according to the present invention is characterized by admixing zeolite particles retaining at least one metal ion having a bactericidal property with a polymer or a mixture of polymers prior to

- 4 -

coating onto a metallic sheet. Preferably, the zeolite particles retain the metal ions having bactericidal properties at ionic exchange sites of the zeolite in an amount less than the ion exchange saturation capacity of the zeolite.

- [0012] In one embodiment, the method of the present invention comprises the steps of (a) cleaning the surface by chemical or mechanical means; (b) surface preparation or pretreatment of the metal surface by coating with a pretreatment layer appropriate to the base metal to gain proper adhesion properties; (c) electrostatically coating the surface of the pretreated metal sheet with a uniform layer of an oxide, phosphate, or zeolite containing resin and (d) subjecting the coated metal article to curing conditions to cure or dry the resin to produce a hardened and adhered coating to the final sheet product.

Brief Description of the Drawings

- [0013] FIG. 1 is a diagrammatic sectional view of a sheet metal according to the present invention.
- [0014] FIG. 2 shows flow chart of the process for producing metal sheets coated with a polymer containing an antimicrobial oxide or zeolite.
- [0015] FIG. 3 is a schematic diagram of the powder coating apparatus used in the present invention.

Detailed Description of the Invention

- [0016] The present invention provides precoated metal sheets such as iron or steel sheets, aluminum sheets, galvanized and aluminized steel sheets, and stainless steel sheets coated with a polymer containing inorganic anti-bacterial particles before the metal sheets are mechanically worked into complex shapes as by die pressing, bending, embossing, rolling, and drawing. The inorganic anti-bacterial particles are metal component-supporting oxides and zeolite powders that are made from

- 5 -

core particles selected from the group consisting of oxides of titanium, aluminum, zinc and copper, sulfates of calcium, strontium and barium, zinc sulfide, copper sulfide, zeolites, mica, talc, kaolin, mullite, zirconium phosphate and silica.

- [0017] For convenience herein, the expression "antimicrobial" or "antibiotic" is used generally to include antibacterial, antifungal, antialgal, antiviral, antiprotozoan and other such activity. The antimicrobial film of the present invention is particularly effective to the following bacteria, fungi and yeast: *Bacillus cereus* var *mycoides*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Streptococcus faecalis*, *Salmonella gallinarum*, *Vibrio parahaemolyticus*, *Candida albicans*, *Streptococcus mutans*, *Legionella pneumophila*, *Fusobacterium*, *Aspergillus niger*, *Aureobasidium pullulans*, *Cheatomium globosum*, *Gliocladium virens*, *Pencillum funiculosum* and *Saccharomyces cerevisiae*.
- [0018] The method of the present invention comprises the steps of (a) cleaning the surface by chemical or mechanical means 40; (b) surface preparation or pretreatment 50 of the metal surface by coating with a pretreatment layer appropriate to the base metal to gain proper adhesion properties; (c) coating 60 the surface of the pretreated metal sheet with a uniform layer of a resin containing a metal component-supporting oxide, phosphate or zeolite powder and (d) subjecting the coated metal article to curing conditions 70 to cure or dry the resin to produce a hardened and adhered coating to the final sheet product.
- [0019] The inorganic anti-bacterial core particles has at least a primary surface coating or constituent, comprising of from about 0.05 to about 20% by weight based on the core particles, of at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures

- 6 -

thereof. Preferably, the coating is at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, or mixtures thereof and mixtures thereof.

- [0020] A coated sheet metal according to the invention, indicated by the general reference 10, can be seen in FIG. 1. As used herein, the term "sheet" or "strip" refers to a length of flat metal material of any width formed in continuous strips or cut to specific lengths. Generally, the sheet is a flat rolled metal product with a width to thickness ratio greater than about 25 and a thickness of less than about 0.250 inches.
- [0021] This sheet 10 comprises a substrate consisting of a metal sheet 12 made from metal or metal alloys selected from the group consisting of aluminum, iron, nickel, titanium, molybdenum, magnesium, manganese, copper, silver, lead, tin, chromium, beryllium, tungsten and cobalt, and alloys of two or more thereof. Examples of the alloys are alloy steels such as carbon steel, nickel steel, chromium steel, nickel - chromium steel, chromium - molybdenum steel, stainless steel, silicon steel and Permalloy; aluminum alloys such as Al-CI, Al-Mg, Al-Si, Al-Cu-Ni-Mg and Al-Si-Cu-Ni-Mg; copper alloys such as brass, bronze, silicon bronze, silicon brass, nickel silver and nickel bronze; nickel alloys such as nickel manganese (D nickel), nickel-aluminum (Z nickel), and nickel-silicon.
- [0022] Further as the aluminum-based metal, there can be used pure aluminum; aluminum oxide; and aluminum alloys for casting and expanding such as Al-Cu, Al-Si, Al-Mg, Al-Cu-Ni-Mg, Al-Si-Cu-Ni-Mg alloys, high tensile aluminum alloy and corrosion resistant aluminum alloy. Also as the iron-based metals, there can be used pure iron, iron oxide, carbon steel, nickel steel, chromium steel, nickel - chromium steel, chromium - molybdenum steel, nickel - chromium - molybdenum steel, stainless steel, silicon steel, Permalloy, non-magnetic steel, magnet steel, cast steel, etc. Preferably, the metal sheet

- 7 -

is selected from the group consisting of stainless steel, carbon steel, iron, aluminum, aluminized steel, galvanized steel, aluminum and steel alloys, magnesium, and magnesium alloys.

- [0023] On one or both of its faces, sheet 12 is coated with an antimicrobial film layer 14 comprising an organic polymer 16. The polymer 16 has inorganic antimicrobial powders 18 dispersed within the polymer comprising an oxide or zeolite core 20 with at least a primary surface coating or constituent of an antimicrobial metal 22.
- [0024] The steels that may be employed for the manufacture of the metal sheet 12 are of various types. One type corresponds to ferritic grade stainless steels that contain 17 wt.% of chromium (Cr) with or without molybdenum (Mo) referred to according to the US Standard as AISI409, AISI 430, AISI 434, AISI 439 and AISI 444, and the French Standard as Z3CTNb18. A second type corresponds to austenitic grades that contain from about 16 to about 18 wt.% of chromium and at least 2 wt.% of nickel (Ni) with or without molybdenum, referred to according to the US Standard as AISI 304 and AISI 316. Other stainless steels can be employed, provided that they contain at least 11 wt.% of chromium. It is possible, for example, to employ a ferritic steel sheet 12 containing, on a mass basis, from about 11 to about 20 wt.% of chromium and from about 0.2 to about 2 wt.% of nickel.
- [0025] In coil-coating processes, a continuous strip of sheet metal is uncoiled at the line entrance and recoiled at the exit, having been coated or otherwise treated. The line speeds can be up to 200 m/min. It is also possible to coat a series of metal blanks removed from the coils.
- [0026] A process that will be described below manufactures the coated sheet metal 10.

1. Surface cleaning

- [0027] A degreasing operation is recommended to guarantee a good adherence of the coating. In fact, if the surface of the metal sheet is not degreased, the fatty substances and other surface contaminants that are not removed are liable to reduce the adherence of the resin coating and to give rise to a nonhomogeneous deposit comprising areas without coating.
- [0028] The metal substrate is desirably free of contaminants, such as petroleum greases and oils, that may cause the pretreatment and coating to be insufficiently adhered to the metal substrate. Consequently, it is desirable, prior to applying the coating composition, to clean the metal substrate. Various methods of cleaning are well known in the art. The particular cleaning method should be able to adequately remove residual oil or dirt from the surface but should not cause over-etching of the metal surface. Exemplary cleaning methods include solvent cleaning (such as a chlorinated solvent (*e.g.*, methylene chloride), ketone (*e.g.*, acetone), alcohol (*e.g.*, methanol), or toluene, emulsion cleaning, alkaline cleaning, acid cleaning, pickling, salt bath descaling ultrasonic cleaning, roughening (*e.g.*, abrasive blasting, barrel finishing, polishing and buffing, chemical etching and electro-etching).
- [0029] The degreasing of the sheet metal is generally performed either chemically or electrolytically. The surface of the work piece of metal may alternatively be cleaned by mechanical means (grinding or sandblasting). The main object of the grinding or sandblasting procedure is to remove impurities or oxides on the surface, to prevent impurities from contaminating the surface alloy layer. In the meantime, the surface roughness will be increased after this procedure, which facilitates the adhesion of coating. Silicon carbonate sandpaper of #180 to #600 is suitable for grinding. Silica sand or other mineral sand can be used in sandblasting. The sheet metal can be degreased

chemically by being placed in contact with a solution containing halogenated organic solvents such as methylene chloride, 1,1,1-trichloroethane, perchloroethylene or trichloroethylene.

- [0030] The degreasing operation may be performed electrolytically in an electrolysis bath or electrolyte consisting of an aqueous solution containing alkaline mixtures similar to those just specified or else calcium carbonate or potassium hydroxide. The electrolyte may contain an alkaline compound in a proportion of from about 0.5 to about 20 wt%. The temperature of the electrolyte may be between from about 25° and about 95°C. The sheet metal may be subjected to a current density of between 0.1 and 20 A/dm² for a period longer than about 0.1 seconds.
- [0031] The sheet metal can also be degreased chemically by employing a solution based on alkaline mixtures containing one or more agents selected from the group consisting of caustic soda, soda ash, alkaline silicates, sodium hydroxide, sodium carbonate, sodium metasilicate, phosphates, alkaline builders, ammonium acid phosphate, ammonium hydroxide, monoethanol amine, and dimethylamine oxide and optionally containing one or more of the agents selected from the group consisting of complexing agents, surfactants, sequestrant, builders, surface-active agents, defoaming agents, and mixtures thereof. The alkaline degreasing solutions and alkaline degreasing agents employed for cleaning metal surfaces are well known in the literature. Exemplary methods will use a solution of potassium or sodium hydroxide at a concentration of from about 1 to about 5 %. The degreasing solution is applied to the surface of the metal sheet by known spray or dip methods. Generally, these are applied at a temperature of from about 50 to about 200°C, preferably from about 60 to about 80°C.

- 10 -

- [0032] Alkaline builders may be generally classified into three types, namely, the strong alkaline type composed mainly of sodium silicate or trisodium phosphate and/or caustic soda, medium alkaline type composed of one or more than one of the following; disodium phosphate, sodium pyrophosphate, sodium carbonate, *etc.*, and mild alkaline type composed of disodium phosphate, sodium bicarbonate, sodium tripolyphosphate, sodium sesquicarbonate, *etc.* Any alkaline builder of the above types may be employed therefor.
- [0033] The temperature of the alkaline solution is generally between about 25° and about 95°C. Preferably, the temperature of the alkaline solution is greater than about 50°C. More preferably, the temperature is greater than about 60°C. The sheet metal is generally subjected to the solution for a period longer than 0.1 second. Preferably, the sheet metal is subjected to the alkaline solution for a period longer than 1 second. More preferably, the sheet metal is subjected to the alkaline solution for a period longer than 3 seconds.
- [0034] The cleaning bath may have any appropriate pH suitable for the process conditions and compatible with the equipment. For example, if the equipment is mild steel that is prone to corrosion under acidic conditions, the pH of the cleaning bath should not be so low as to cause acid corrosion. The cleaning bath may be mildly acidic if ammonium acid phosphate is selected as the cleaning agent and, more specifically, has a pH of from about 2.0 to about 7.5, preferably the agent has a pH of from about 2.0 to about 5.5, more preferably the agent has a pH of from about 2.0 to about 3.5. Alternatively, the cleaning bath may be mildly alkaline if ammonium hydroxide is selected as the cleaning agent and, more specifically, has a pH of from about 7.0 to about 12, preferably the agent has a pH of from about 7.0 to about 11, more preferably the agent has a pH of from about 8.0 to about 10.0.

- [0035] The concentration of the cleaning agent and the surfactant must be sufficient to remove substantially all oil and other contaminants from the metal surface, but must not be so high that a significant amount of foaming occurs. Typically, the water rinse step may be avoided if the cleaning bath is not too concentrated, which is acceptable in the event that the metal is initially relatively clean.
- [0036] The metal surface having been contacted by the cleaning solution is generally rinsed with water (neutral medium) or other known rinse agent, also by known spray or dip methods. Air-drying or other drying means generally follows rinsing.
- [0037] The surface cleaning step may be eliminated or combined with the surface pre-treatment step in certain circumstances depending upon the condition of the metal and the type of pre-treatment utilized.

2. Surface Pre-Treatment

- [0038] The metal sheet is preferably pretreated to enhance the adhesion of the coating composition after curing. The pretreatment may be, for example, the formation of an interlayer on the metal substrate surface that enhances adhesion of the coating composition after curing. For example, the interlayer may be a chemical conversion layer (*i.e.*, coating), such as a silane, phosphate, chromate, epoxy, or oxide coating or the interlayer may be an adhesive coating. Generally, the pretreatment is by contacting the metal with chromium phosphate, chromium chromate, zinc phosphate, iron phosphate, or an organic epoxy-based composition.
- [0039] The interlayer may be any thickness sufficient to enhance the adhesion of the coating composition during application and after curing but, in general, the interlayer is at most about 100 percent of the thickness of the cured coating of the antimicrobial composition on one side,

- 12 -

preferably the interlayer is at most about 50 percent of the thickness of the cured coating of the antimicrobial composition, and more preferably the interlayer is at most about 10 percent of the thickness of the cured coating of the antimicrobial composition. The interlayer, typically, is between about 0.01 to about 30 microns thick. Preferably thickness of the interlayer is at least about 0.1 microns, more preferably at least about 0.2 microns and most preferably at least about 0.5 microns. Preferably the thickness of the interlayer is at most about 20 microns, more preferably at most about 15 microns and most preferably at most about 10 microns.

- [0040] Generally, the metal surface is pretreated with an aqueous composition comprising phosphoric acid and a divalent metal ion when the metal substrate is steel, zinc or zinc based alloys or zinc aluminum alloy coated steel, aluminum or aluminum alloy. Any divalent metal ion may be used as the divalent metal ion for use in the composition. Generally, the metal is selected from the group consisting of divalent transition metal ions, such as Mn, Co, Fe, Ni, and Zn, and alkaline earth divalent metal ions, such as Mg, Ca, Sr, and Ba. Preferably the divalent metal ion is other than nickel for environmental reasons. Preferably the metal is selected from the group consisting of Fe, Ni and Zn. Most preferably, the metal is Zn. Silicate may be added to precipitate out any titanium ions that can then be removed from the phosphating composition.
- [0041] To accelerate the formation of the phosphate layer, oxidants such as bromate, chlorate, nitrate, nitrite, organic nitro compounds, perborate, persulfate or hydrogen peroxide, m-nitrobenzene sulfonate, nitrophenol or combinations thereof may be added.
- [0042] To optimize the layer formation on certain materials, there is for instance added sulfate, simple or complex fluoride ions, silicofluoride, boron fluoride, citrate, tartrate, hydroxy-carboxylic acids,

- 13 -

aminocarboxylic acids, condensed phosphates, or SiO-containing compounds (e.g., alkali metal metasilicate, alkali metal orthosilicate, and alkali metal disilicate) and mixtures thereof.

- [0043] When the metal surface is predominantly galvanized metal and/or steel, the pretreatment comprises contacting the metal surface with an aqueous composition comprising phosphoric acid and a divalent metal ion, the composition generally having a total phosphate content from about 0.01 to about 3 moles/liter, preferably a total phosphate content from about 0.02 to about 2 moles/liter, and more preferably a total phosphate content from about 0.1 to about 1 moles/liter. The composition also generally having divalent metal ion content of from about 0.001 to about 2 moles/liter (based on metal ion content), preferably a metal ion content of from about 0.01 to about 1 moles/liter, and more preferably a metal ion content of from about 0.05 to about 0.5 moles/liter.
- [0044] In case of an aluminum, aluminum alloy, or aluminized steel sheet, in order to enhance corrosion resistance, surface hardness and adhesive property of the substrate, it is preferable to form an oxide film (alumite) on the sheet by pretreatment (anodizing) with caustic soda, oxalic acid, sulfuric acid or chromic acid.
- [0045] The quantities of the components in the composition can vary but are preferably chosen to suit the particular metal which is prevalent in the surface being treated and therefore depends upon whether the metal surface being treated is mainly steel, galvanized, aluminum or a aluminum/zinc alloy.
- [0046] In particular, for use on aluminum surfaces, it is preferable that the aqueous composition should also include an activator preferably fluoride ions. Generally fluoride ions will be provided in the form of hydrogen fluoride. Fluoride is generally present in amounts up to 1.0

- 14 -

moles/liter, preferably in amounts up to 0.5 moles/liter, and more preferably in amounts up to 0.25 moles/liter.

- [0047] In particular in the compositions for pretreatment of galvanized metals or steel metal surfaces, preferably the composition also includes boric acid. When the prevalent metal surface for coating is galvanized, boric acid is generally present in an amount of at least 0.02, preferably in an amount of at least 0.05, and more preferably in an amount of at least 0.1.
- [0048] In particular in the compositions for pretreatment of stainless steel metals or stainless steel metal surfaces, preferably the surface pretreatment is an epoxy or other organic based pretreatment.
- [0049] The pretreatment compositions can be prepared by the addition of the components in any convenient order. The phosphating is generally aimed at providing a fast and efficient treatment for a coil coating metal conversion process.
- [0050] For coil coating, the pretreatment coating is generally applied by roll coating or reverse roll coating, or by passing the metal sheet through a spray or bath of the composition. However, any other standard application form can be used such as by spraying or conventional spray/dip treatment. Preferably, phosphate pretreatments will be by dip treatment and epoxy pretreatments will be by roll coating. The applied pretreatment should cover any desired area of the metal substrate to be coated by the final antimicrobial polymer.
- [0051] The sheet metal is generally subjected to the solution for a period longer than 0.1 second. Preferably, the sheet metal is subjected to the alkaline solution for a period longer than 1 second. More preferably, the sheet metal is subjected to the pretreatment solution for a period longer than 10 seconds.

- 15 -

- [0052] The pretreatment of the metallic sheet is generally followed by a rinsing with water or other neutral rinse medium by known spray or dip methods to remove residual pretreatment solution. This stage is optionally used to ensure removal of any pretreatment residues or to seal or cure the pretreatment surface with a final rinse agent. Air-drying or other drying means generally follows rinsing.
- [0053] The pretreatment is generally dried by heating and this may be carried out by conventional means, for example by passing the coil or coated article through an oven or exposing to IR radiation. The drying temperature is generally between about 25° and about 95°C. Preferably the temperature reached on drying or curing is at least 50°C. More preferably the temperature reached on drying or curing is at least 60°C. Once the coated metal surface has been dried, the antimicrobial coating can be immediately applied.

3. Coating Composition

- [0054] The antimicrobial coatings of the present invention are organic polymer compositions containing antimicrobial metal-supporting oxide, phosphate or zeolite particles.
- [0055] To prepare the coating composition, any sequence of mixing the constituents sufficient to form the coating composition may be employed. The mixing or emulsification technique employed may be any suitable technique, such as those known in the art. Exemplary mixing techniques include ball, bead or sand milling, high shear mixing, sonic mixing, attritor milling and rapid shaking.

a. Inorganic Anti-Bacterial Particles

- [0056] The inorganic anti-bacterial particles are metal component-supporting oxides and zeolite powders that are core particles selected from the

group consisting of oxides of titanium, aluminum, zinc and copper, sulfates of calcium, strontium and barium, zinc sulfide, copper sulfide, zeolites, mica, talc, kaolin, mullite, silica, zirconium and zirconium phosphate.

- [0057] The inorganic anti-bacterial core particles have at least a primary surface coating or constituents, comprising of from about 0.05 to about 20% by weight based on the core particles, of at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures thereof. Preferably, the coating is at least one metal or metal compound having antimicrobial properties selected from the group consisting of silver, copper, zinc, or mixtures thereof and mixtures thereof. Preferably, the amount of antimicrobial component on or in the core particle is at least about 0.1% by weight, more preferably at least about 0.2% by weight, and most preferably at least about 0.5% by weight. Preferably, the amount of antimicrobial component on or in the core particle is at most about 20% by weight, more preferably at most about 15% by weight, and most preferably at most about 10% by weight.
- [0058] The inorganic anti-bacterial metal component-supporting oxides and zeolite may additionally be coated with a secondary, protective layer selected from the group consisting of silica, silicates, silicon dioxide, borosilicates, aluminosilicates, alumina, aluminum phosphate, zinc, zinc oxide, zinc silicate, copper, copper oxide, silanes, and mixtures thereof, among others. The secondary protective layer normally comprises from about 0.1 to about 20% by weight. Preferably, the amount of secondary protective coating layer on the metal-containing particle is at least about 0.5% by weight, more preferably at least about 0.2% by weight, and most preferably at least about 1.0% by weight of the coated particle composition. Preferably, the amount of secondary

- 17 -

protective coating layer on the metal-containing particle is at most about 10% by weight, more preferably at most about 5% by weight, and most preferably at most about 3% by weight of the coated particle composition.

- [0059] It will be appreciated by those skilled in the art that if relatively fine core particles are employed when practicing the invention, then the practitioner should ensure substantially total surface coverage of the first coated core material. While the protective layer can be quite dense, the protective layer should be sufficiently porous to permit diffusion of the antimicrobial component through the coating at an effective rate and function as a barrier that limits, if not eliminates, interaction between the antimicrobial component and a surrounding matrix.
- [0060] The inorganic anti-bacterial metal component-supporting oxides and zeolites, with or without a secondary, protective layer, may additionally be coated with a dispersion enhancing coating such as a suitable resin or a hydrous metal oxide, *e.g.*, alumina, hydrous alumina, zirconia, mixtures thereof, among others. This coating corresponds to about 0.1% to at least about 5% by weight and normally about 0.5 to about 3% by weight based on the core material.
- [0061] The amount of a dispersion aid that is present in the antimicrobial composition ranges between about 0.1% and at least about 2.0% by weight based upon the antimicrobial powder, with about 0.5% to about 1% by weight normally being effective.
- [0062] It will be appreciated by those skilled in the art that the ratio of the secondary coatings and dispersion aids can vary widely and may be readily selected by the artisan.
- [0063] The process for preparing the inorganic anti-bacterial metal component-supporting oxide composition of the invention is described

- 18 -

in greater detail in U.S. Pat. No. 5,180,585; the disclosure of which is incorporated herein by reference.

- [0064] Preferably, the inorganic antibiotic particle is an antibiotic zeolite. The “antibiotic zeolites” used in the invention are those of which ion-exchangeable ions are partially or completely ion-exchanged with antibiotic ions. Antibacterial metal-supporting zeolite is known per se and may be prepared by ion-exchanging zeolite with antibacterial metals. Examples of the antibacterial metals include silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures thereof. Preference is given to silver, copper, zinc, or mixtures thereof. Particularly, silver alone or a combination of silver with copper or zinc is excellent in antibacterial properties. Methods for preparing antibacterial zeolite are described in, for example, U.S. Pat. Nos. 4,525,410, 4,741,779, 4,775,585, 4,906,466, 4,911,898, 4,911,899, 4,938,955, 4,938,958, 5,503,840, 5,180,585, 5,556,699, 5,595,750, 6,071,542, incorporated herein by reference in their entirety.
- [0065] Such zeolites have been incorporated in antibiotic resins (as shown in U.S. Pat. Nos. 4,938,955 and 4,906,464) and polymer articles (U.S. Pat. No. 4,775,585) while other uses are described in U.S. Pat. Nos. 5,714,445; 5,697,203; 5,562,872; 5,180,585; 5,714,430; and 5,102,401, all incorporated herein by reference in their entirety.
- [0066] In the antibiotic film of this invention, either natural or synthetic zeolites may be used as the “zeolite component”. Zeolites are aluminosilicates, of either natural or synthetic origin, which have sites at which cationic exchange may occur. By treating them with solutions of metal ions, a desired antimicrobial metal ion can be substituted in the zeolite structure.

- [0067] Zeolite is generally aluminosilicate having a three dimensionally grown skeleton structure and is generally represented by $XM_{2/n}Al_2O_3 \cdot YSiO_2 \cdot ZH_2O$, written with Al_2O_3 as a basis, wherein M represents an ion-exchangeable metal ion, which is usually the ion of a monovalent or divalent metal; N corresponds to the valence of the metal; X is a coefficient of the metal oxide; Y is a coefficient of silica; and Z is the number of water of crystallization. There are known various kinds of zeolites having different component ratios, fine pore diameters, and specific surface areas. As the zeolite used in the present invention, any natural or synthetic zeolites can be used.
- [0068] Examples of natural zeolite include analcime, chabazite, clinoptilolite, erionite, faujasite, mordenite, and phillipsite. On the other hand, typical examples of synthetic zeolite include A-type zeolite, X-type zeolite, Y-type zeolite, and mordenite. A synthetic zeolite is preferably used as the zeolite in the present invention. As already mentioned above, the antibiotic zeolites as used herein are those of which ion-exchangeable ions such as sodium ions, potassium ions, calcium ions, magnesium ions and iron ions are partially or completely ion-exchanged with the aforementioned antibiotic metal ions such as silver, copper or zinc ions or mixtures thereof.
- [0069] The shape of zeolite may preferably be powdery particulate. A particle size of the zeolite can suitably be selected depending on application. For films of the present invention, the average particle size is generally 10 microns or less, preferably the average particle size is 6 microns or less, more preferably the average particle size is 5 microns or less. For films of the present invention, the average particle size is generally 0.1 microns or more, preferably the average particle size is 0.2 microns or more, more preferably the average particle size is 0.5 microns or more.
- [0070] The metal is preferably supported on solid particles of zeolite through an ion-exchange reaction. Zeolite is preferably ion-exchanged with

- 20 -

metal ions in an amount of less than an ion-exchangeable amount of the zeolite particles, particularly in an amount less than about 100%, preferably in an amount less than about 90%.

- [0071] It should be understood that the amount of the metal incorporated in the metal-zeolite might vary depending upon the metal used and whether or not combinations of metals are used. In the case of silver alone, the amount of the metal incorporated in the metal-zeolite is generally 20% by weight or less, preferably from about 0.001 to about 15% by weight, more preferably from about 0.01 to about 10% by weight, most preferably from about 0.05 to about 5% by weight, based on anhydrous zeolite plus metal.
- [0072] In the case of zinc or copper, the amount of zinc or copper incorporated in the metal-zeolite is generally 25% by weight or less, preferably from about 0.001 to about 20% by weight, more preferably from about 0.01 to about 15% by weight, most preferably from about 0.05 to about 10% by weight, based on anhydrous zeolite plus metal. It is possible to use two or more of silver, copper, zinc and the other metal ions together. In this case, although the total amount of the metal ions is dependent on the composition of the metal ions, it is generally 25% by weight or less, preferably from about 0.001 to about 20% by weight, more preferably from about 0.01 to about 15% by weight, most preferably from about 0.05 to about 10% by weight, based on anhydrous zeolite plus metal.
- [0073] It is possible to also incorporate other ions than the antibacterial metal ions, for example, sodium, potassium, magnesium, calcium, aluminum, titanium, cerium and other metal ions. Accordingly, these ions may remain or co-exist.
- [0074] After drying, the antibiotic zeolites thus obtained are pulverized and classified and then are incorporated into a desired resin.

b. Polymers

[0075] The metal coating compositions are generally based on polymer resins such as aminoalkyd resins, aminoacrylic resins, epoxy resins, and polyurethane resins. In the present invention, the organic polymeric materials used for forming antibiotic-containing films may be any synthetic, natural or semi-synthetic organic polymers so far as they can be formed into films. Generally, such polymers are thermoplastic polymers or thermoset polymers. Examples of such organic polymeric materials include, but are not limited to, acetate rayon, acrylic resins, acrylonitrile-butadiene-styrene (ABS) resins and acrylic resins, aliphatic and aromatic polyamides, aliphatic and aromatic polyesters, allyl resin, (Allyl), AS resins, butadiene resins, chlorinated polyethylene, conductive resins, co-polymerized polyamides, copolymers of ethylene and vinyl acetate, cuprammonium rayons and natural and synthetic rubbers, EEA resins, epoxy resins (*e.g.*, bisphenol, dihydroxyphenol, and novolak), ether ketone resins, ethylene vinyl alcohol, (E/VAL), fluorine resins, fluorocarbon polymers, fluoroplastics, (PTFE), (FEP, PFA, CTFE, ECTFE, ETFE), high density polyethylenes, ionomer resins, liquid crystal polymer, (LCP), low density polyethylenes, melamine formaldehyde, (melamine resins), natural polymers such as cellulosics, nylons, phenol-formaldehyde plastic, (PF) phenolic resins, polyacetal, (acetal), polyacrylates, (acrylic), polyacrylonitrile, (PAN), (acrylonitrile), polyamide, (PA), (nylon), polyamide-imide, (PAI), polyaryletherketone, (PAEK), (ketone), polybutadiene, (PBD), polybutylene terephthalate, polybutylene, (PB), polycarbonate, (PC), polycarbonates, polydicyclopentadiene, (PDCP), polyketones, (PK), polyester block copolymers, polyesters, polyesterurethane, polyesterurethaneurea, polyether and polyester block polymers, polyether ketoneketone (PEKK), polyetherether ketone (PEEK),

- 22 -

polyetherimide, (PEI), polyethers, polyethersulfone, (PES), polyetherurethane, polyetherurethaneurea, polyethylene isophthalate, polyethylene terephthalate, polyethylene, (PE), polyethylenechlorinates, (PEC), polyglycolic acid, polyhexamethylene terephthalate, polyimide, (PI), polylactic acid, polymethylpentene, (PMP), poly-m-phenylene isophthalamide, polyolefins, polyphenylene oxide, (PPO), polyphenylene sulfide, (PPS), polyphthalamide, (PTA), poly-p-phenylene terephthalamide, polypropylene, (PP), polysiloxanes such as polydimethyl siloxane, polystyrene, (PS), polysulfides, polysulfone, (PSU), polytetrafluoroethylene, polyurethane, (PU), polyvinyl acetate, polyvinyl alcohols, polyvinylchloride, (PVC), polyvinylidene chloride, (PVDC), polyvinylidene fluoride and polyvinyl fluoride, rayon, reconstituted silk and polysaccharides, reinforced polyethylene terephthalate resins, segmented polyurethane elastomers, silicone resins, spandex or elastane elastomers, styrene type specific resins, thermoplastic polyurethane elastomers, thermosetting synthetic polymers such as phenol-formaldehyde copolymer, triacetate rayon, unsaturated polyester resins, urea resins, urethane resins, vinyl chloride resins, vinyl polymers, and vinylidene chloride resins. This group includes reasonable copolymers, terpolymers and mixtures of the species listed.

- [0076] Examples of powder coating raw materials suitable for use in the present invention include thermoplastic and thermoset base resins.
- [0077] Thermoplastic resins suitable for use in the coating powders of this invention must melt and flow out to a thin film within a few minutes at application temperatures of from 30°C to about 350°C without significant degradation. Examples of suitable thermoplastic resins for use in the practice of the invention include polyamides, polyesters, cellulose esters, polyethylene, polypropylene, poly(vinyl chloride) or PVC, poly(vinylidene fluoride) or PVF₂, polyphenylsulfones and poly

(tetrafluoroethylene) or PTFE. It is to be appreciated that as a result of the typically lower processing temperatures to which resins are subjected to in the practice of the invention, thermoplastic resins such as polyphenylsulfones and PTFE are particularly suited for processing in accordance with the invention.

- [0078] Plasticization of PVC has been the conventional way to lower its melt viscosity so that it will flow sufficiently when heated to form a continuous film. Nylon-11 and nylon-12 resins are representative of the polyamides and cellulose acetate butyrate is an example of the cellulose esters contemplated for use in this invention. All of the suitable thermoplastic resins are available commercially from numerous sources.
- [0079] The thermosettable resins which are suitable for this invention include epoxy resins, polyurethanes, silicones, polyesters (including unsaturated polyesters), acrylics, and hybrids such as epoxy-acrylic, polyester-acrylic, and epoxy-polyester. The glass transition temperature (T_g) of these resins must be high enough that the particles do not fuse together or sinter at temperatures likely to be encountered during transportation and storage. Preferably, the T_g is at least about 30°C.
- [0080] The epoxy resins are those containing aliphatic or aromatic backbones with oxirane functionality and are exemplified by the diglycidyl ether condensation polymers resulting from the reaction of epichlorohydrin with a bisphenol in the presence of an alkaline catalyst. Bisphenol A is most commonly used but the bisphenols B, F, G and H are also suitable. These are available from a wide variety of commercial sources. The GT-series of bisphenol A epoxies from Ciba-Geigy, including 7004, 7013, 7014, 7074, and 7097 are examples of useful epoxy resins in this invention. Shell Chemical Co. also supplies suitable epoxy resins under its EPON trademark.

- 24 -

- [0081] Dicyandiamide, modified and substituted dicyandiamides, solid dicarboxylic acids and their anhydrides are examples of the many agents that may be used for the curing of epoxy resins. A curing agent in solid form is preferred for convenience in the formulation of epoxy resin-based powders as well as in the formulation of other resin-based powders in this invention.
- [0082] Hydroxy functional polyesters are predominantly hydroxyl in functionality; their acid number is preferably about 15 or less and, even more preferably, from about 1 to 2. The hydroxyl number, on the other hand, is preferably from about 25 to about 50, as conventionally reported. The Tg is preferably higher than 30°C. because of its effect on the blocking problem. Hydroxy functional polyesters are commercially available under the trademarks RUCOTE 107, CARGILL 3000, CARGILL 3016, and CRYLCOAT 3109.
- [0083] The hydroxyl-functional polyesters are curable through the hydroxyl groups with aminoplasts and with aliphatic and aromatic isocyanates. Isocyanate curing forms resins that technically are polyurethanes but are often sold as polyesters. Hexamethoxymethyl melamine and tetramethoxy glycoluril exemplify said etherified forms. Thus, a wide variety of commercially available aminoplasts and their precursors can be used for combining with the linear polyesters of this invention. Particularly preferred are the amino cross-linking agents sold by American Cyanamid under the trademark CYMEL. In particular, the CYMEL 301, CYMEL 303, and CYMEL 385 alkylated melamine-formaldehyde resins are useful. Of course, it is possible to use mixtures of all of the above N-methylol products.
- [0084] Aminoplast curing agents are generally provided in an amount sufficient to react with at least one-half the hydroxyl groups of the polyester, *i.e.*, be present at least one-half the stoichiometric equivalent of the hydroxyl functionality.

- 25 -

- [0085] Acidic catalysts may be used to modify the curing of the polyester with an aminoplast resin by lowering the required temperature or raising the reaction rate or both.
- [0086] The diisocyanates cure the hydroxy-functional polyester resin by forming urethane linkages between the polymer chains at the hydroxyl group sites. Examples of commercially available curing agents of this type are the 24-2400, 24-2430, and 24-2450 products sold under the CARGILL trademark.
- [0087] Carboxyl-functional polyesters are also suitable for the purposes of this invention. They may be made from the same polyfunctional acids and glycols as are the hydroxyl-functional polyesters but with an excess of the acids. The acid number is from about 18 to about 55. They are exemplified by products sold under the trademarks CRYLCOAT 430, CRYLCOAT 3010, URALAC 3400, URALAC 3900, and GRILESTA V7372, which has a Tg of about 60°C. and an acid number of from about 32 to about 35, and which is sold by Ems-Chemie AG. Fast cures are achieved with polyepoxide curing agents such as triglycidyl isocyanurate (TGIC).
- [0088] Unsaturated polyesters suitable for use in the practice of the invention include ethylenically unsaturated reaction products of an organic di or polyfunctional acid and a di or polyfunctional alcohol. Typically the acid is unsaturated. Such polyester resins typically work best in combination with a copolymerizable second resin such as diallyl phthalate. Initiators may also need to be incorporated.
- [0089] A hybrid resin system is typically considered a mixture of a carboxyl-functional polyester and an epoxy resin. The acidic polyester suitably has an equivalent weight of 550-1100 and the epoxy resin has an equivalent weight of 600-1000. Zinc oxide is effective as a catalyst at 1-5 parts per hundred parts by weight of the resins to improve the cure

- 26 -

rate and physical properties of the product. Other hybrid resin systems such as the epoxy-acrylic and polyester-acrylic mixtures mentioned above are also suitable for this invention.

- [0090] The preferred acrylic resins for coating powders are copolymers of alkyl acrylates and/or methacrylates with glycidyl-methacrylates and/or acrylates and olefinic monomers such as styrene. Hydroxyalkyl acrylate and methacrylate copolymers are also suitable for this invention. Suitable silicone resins for use in this invention should be solid at room temperature and preferably have a Tg of at least about 45°C. Suitable silicone resins are also described in U.S. Pat. Nos. 3,170,890 and 4,879,344 3,585,065 and 4,107,148, the teachings of which are incorporated herein by reference. Further, crystalline resins, such as the crystalline polyester PIONEER PIOESTER 4350-55, can also be used.
- [0091] The polymer is usually in the form of a powder or pellet. In accordance with the invention, any suitable polymer may be selected by one skilled in the art which is capable of functioning as a matrix for the antimicrobial agents used (and other optional ingredients) and coating the specified sheet metals. It is evident that depending on the particular application or use and other pertinent considerations, an appropriate choice of polymer can readily be made.
- [0092] The organic polymer acts as a carrier and matrix for the oxides and zeolites further described herein and also as a protective barrier coating for the sheet metal substrates.
- [0093] Admixing the antibiotic zeolite and an organic polymeric compound in a usual manner and then coating the mixture obtained onto the metallic sheet (forming it into films) can produce the coated products of the present invention. The formation of the film can be carried out according to any known methods for roll coating polymer coatings.

- [0094] Solvents (or liquids to disperse the polymer) which are useful in accordance with the invention include but are not limited to aliphatic hydrocarbons, aromatic solvents, alcohols and other oxygenated solvents, substituted hydrocarbons, phenols, substituted aromatic hydrocarbons and halogenated aliphatic hydrocarbons. Each resin system has a group of solvents and diluents compatible with the resin and suitable for film forming. In some cases the organic solvent is only used to disperse the resin powder. It is contemplated that water can be used as solvent/diluent or dispersant for some resin compositions.
- [0095] The polymer coatings according to the present invention may contain other additives as well as antimicrobial compositions. They may contain, for example, polymerization catalysts, stabilizers, delustering agents, optical whitening agents, organic or inorganic pigments, inorganic fillers, plasticisers and so on. It is also possible that the antimicrobial particles themselves can fulfill a dual role and provide the benefits of some of the aforementioned additives.
- [0096] To the present antibacterial zeolite may be added white pigments such as magnesium oxide, calcium oxide, aluminum oxide, zinc oxide, titanium oxide, titanium dioxide, silicon dioxide, calcium carbonate, magnesium carbonate and barium sulfate. In addition, to the present antibacterial oxide or zeolite may be added additives such as magnesium silicate, aluminum silicate, zinc silicate, silica gel-zinc, synthetic hydrotalcite, aluminum tripolyphosphate.
- [0097] Conventional procedures for incorporating powders in polymer compositions may be used to prepare the polymer articles of the invention. The antimicrobial powders may be added to a monomer or to an intermediate product prior to polymerization. However, generally they are mixed or compounded with a finished powdered polymer before it is applied as a film. Precoating of antimicrobial particles with polymer greatly facilitates incorporation of the particles in the bulk

polymer. This may be done, for example, by slurring the antimicrobial powder with a solution of the polymer, then removing the solvent by drying. From about 0.1 to about 10% by weight of polymer based on the coated powder and preferably from about 0.5 to about 5% by weight of polymer based on the coated powder is suitable for this purpose.

- [0098] In another embodiment, the coating is placed onto a metal sheet wherein the coating composition is comprised of dispersed epoxy resin particles. Preferably, the metal sheet treated with an epoxy pretreatment is stainless steel or aluminum. The epoxy resin may be a solid or liquid epoxy resin. Preferably the epoxy resin is a powder. Exemplary epoxy resins include diglycidyl ether of bisphenol A, such as those available from The Dow Chemical Company, Midland, Mich. under the trade name D.E.R., and from Shell Chemical Company, Houston, Tex. under the trade name EPON or EPI-REZ and phenol and cresol epoxy novolács, such as those available under the trade name D.E.N. from The Dow Chemical Company, Midland, Mich. Other examples of useful epoxy resins include those described in U.S. Pat. Nos. 5,118,729, 5,344,856 and 5,602,193, each incorporated herein by reference. The amount of epoxy resin in the coating composition may be any amount sufficient to coat a metal substrate that, subsequently, can be cured to form a corrosion resistant coating on the metal.
- [0099] The epoxy coating composition may also contain a surfactant that forms an epoxy resin in water dispersion, wherein the epoxy resin molecules have a neutral or positive surface charge, the surfactant being a nonionic surfactant, amphoteric surfactant or mixture thereof. The nonionic surfactant may be, for example, a nonionic surfactant or combination of surfactants known to form oil in water emulsions. Exemplary nonionic surfactants include polyglycol ether of an epoxy,

an alcohol, fat, oil, a fatty acid, a fatty acid ester or an alkylphenol. Exemplary amphoteric surfactants include those known in the art, such as alkyl betaines and dihydroxyethyl glycinate.

- [00100] The amount of surfactant present in the coating composition may be any amount sufficient to disperse the epoxy resin and cause the epoxy resin particles in the dispersion to have a neutral or positive charge. Generally, the amount of surfactant is at least about 0.1 percent by weight, preferably is at least about 0.5 percent by weight. Generally, the amount of surfactant is at most about 10 percent, preferably is at least about 5 percent by weight of the total coating composition weight.
- [00101] The epoxy coating composition optionally also contains a latent curing agent. Examples of latent curing agents include dicyandiamide and blocked isocyanates, such as an alcohol-blocked toluene diisocyanate. Preferably the latent curing agent is dicyandiamide. The amount of latent curing agent is an amount sufficient to cure the epoxy resin and generally should be an amount that is not so great that the coating, after curing, fails to provide improved corrosion resistance of a metal substrate. Generally, the amount of latent curing agent is at least about 0.1 percent by weight, preferably is at least about 0.5 percent by weight. Generally, the amount of surfactant is at most about 10 percent, preferably is at least about 5 percent by weight of the total coating composition weight.
- [00102] The aqueous epoxy coating composition, of course, contains water in an amount sufficient, for example, to provide an epoxy in water emulsion when the epoxy is a liquid. The water should also be sufficiently pure to provide a water matrix that fails to cause coagulation of the particles (*e.g.*, epoxy or filler particles) due, for example, to impurities (*e.g.*, ionic impurities).

c. Additional Additives

- [00103] The polymer film compositions of the present invention may be clear or may contain pigment particles or dyes. The pigment particles are preferably titanium dioxide, alumina or silica. Preferably, pigment particles are titanium dioxide particles are from about 0.1 to about 10 microns in median particle size, preferably from about 0.2 to about 5 microns in median particle size.
- [00104] Rheology control agents may also be added to keep the powder suspended and provide the proper rheology for spray applications. The rheology control agent may be anionic, nonionic or cationic. The rheology control agent is determined by the composition of the powder coating, and such information is readily available to one skilled in the art. The rheology control agent is added in an amount between 0.50 and 3.0% by weight based on total slurry coating weight.
- [00105] Powder coatings of the present invention may also be used to formulate primers and colored basecoats with metallic effects. Primer or other pigmented coatings are formulated by adding the necessary pigments during the dry mix step prior to extrusion.
- [00106] Powder coating compositions as described herein are useful for both basecoat and clearcoat applications. The resultant coating compositions can form smooth films with a varying degree of gloss.
- [00107] The coating may further be comprised of fillers that impart, for example, opacity or improved wear resistance to the coating composition after it has been cured. Exemplary fillers include ceramic particles or whiskers and known surface treated metal pigments. Preferably the filler is a ceramic selected from the group consisting of oxides, borides, nitrides, carbides, hydroxides, carbonates, silicides, silicates and alloys thereof.

- [00108] When the coating composition contains the filler, the filler is generally present in an amount of about 1 percent to about 50 percent by weight of the total coating composition weight. Preferably the amount of the filler, when present, is at least about 2 percent, more preferably at least about 5 percent. Preferably the amount of the filler, when present, is at most about 40 percent, more preferably at most about 35 percent.
- [00109] If desired, the coating composition may also contain a cross-linking catalyst, for example, to increase the rate of cross-linking (*i.e.*, cure) of the epoxy at a temperature. Generally, the catalyst may be, for example, a tertiary amine or imidazole. Examples of the catalyst that may be employed in the coating composition include 2-methylimidazole, benzylidemethylamine, dimethyl aminomethyl phenol and tris(dimethylaminomethyl)phenol. Preferably the catalyst is 2-methylimidazole.
- [00110] When the coating composition contains the catalyst, the catalyst is generally present in an amount of about 0.001 percent to about 1 percent by weight of the total coating composition weight. Preferably the amount of the catalyst, when present, is at least about 0.002 percent, more preferably at least about 0.005 percent and most preferably at least about 0.01 percent to preferably at most about 0.7 percent, more preferably at most about 0.5 percent and most preferably at most about 0.3 percent by weight of the total weight of the coating composition.
- [00111] If necessary or desired, the coating composition may also contain a small amount of defoamer. The defoamer may be any suitable defoamer, such as those known in the art. Exemplary defoamers include siloxane-based defoamers. The defoamer, when present, is present only in a quantity necessary to control the foaming of the coating composition, since it has been found that, in general, the defoamer impedes the adherence of the coating composition to a metal

- 32 -

substrate. The amount of defoamer, when present, is generally present in an amount of at most about 0.15 percent, more preferably at most about 0.05 percent and most preferably at most about 0.02 percent by weight of the total weight of the coating composition.

4. Coating Application

- [00112] The pretreated metal sheet is then coated with an antimicrobial polymer composition that includes inorganic antimicrobial particles dispersed in an organic polymer. Exemplary coating polymers are the epoxies, polyvinyl chloride, acrylics, polyurethanes, fluorocarbons, and polyesters. The suitable epoxies include phenolic-modified epoxies, polyester-modified epoxies, epoxy-modified polyvinyl chloride, epoxy melamines and cross-linkable epoxies.
- [00113] The powder coatings of this invention can then be applied to the substrate by any conventional powder coating technique, although electrostatic application, *e.g.*, electrostatic spraying, is generally preferred. In electrostatic spray coating, electrostatic spray booths are normally employed which house banks of corona discharge or triboelectric spray guns and a reclaim system for recycling the overspray powders into the powder feed.
- [00114] The most common method for the application of powder coatings is by electrostatic spraying. The basic principle of this method involves propelling the powder, via compressed air, through a spray gun where it becomes electrostatically charged. In addition to charging the powder the gun also serves to deposit the powder supplied by the feeder. When the electric field is removed, the charged particles are still held on the surface, attracted by charges on the substrate. The uncharged powder in the overspray is collected and reused.

- 33 -

- [00115] Another commonly used method of powder coating is triboelectric spraying. This is similar to electrostatic spraying, except the particles are positively charged (electrostatically charged particles have a negative charge).
- [00116] Another technique that can be used for flat surfaces such as the metal strip in the present invention, employs electromagnetic brush technology which enables efficient high speed application of very thin layers with no recycling. In one embodiment, the strip can be passed through a cloud of powder created by a brush delivery system. The powder is then directed over a series of corona wires that charge the powder.
- [00117] Powder coating formulations that do not require curing agents can be applied via the aforementioned electrostatic or tribostatic spray techniques. However, most thermoplastic powder is applied by passing the heated substrate through a fluidized bed.
- [00118] The powder coating can also be applied utilizing a standard cathodic arc plasma physical vapor deposition (PVD) process utilizing an electric arc to create the plasma. In the PVD process, the metal substrate is mounted in an electric arc PVD chamber, a vacuum is created, and the deposition process is conducted. After the PVD process is finished, the article is cooled and dismounted from the PVD chamber, and the metal strip article, having the cured powder coating, is complete.
- [00119] Other conventional techniques can be adopted to include electrostatic or thermal fluidized bed, knife coating, gravity feed and water suspended powder spray methods.
- [00120] Optionally, the substrate is heated, at least one surface, at the time of application and/or subsequently to a temperature equal to or above the temperature needed to cure the powder coating and below the substrate

outgassing and/or degradation temperature, so that the coating particles sufficiently melt, flow and form a smooth continuous coating film, and then cure to a thermoset state or dry to a thermoplastic state without degrading the substrate.

- [00121] Heating can be performed in infrared, convection ovens, induction or a combination of these, although convection ovens are preferred. Time and temperature of the final cure will vary somewhat depending on the coating powders employed and conditions of use. However, regardless of cure time and temperatures employed, provided that the powder ingredients have been sufficiently flowed onto the substrate before curing, the coating films generated on the substrates will have a visually consistent appearance and will be without entrapped bubbles that interfere with the aesthetic appearance and distinctness of image required by conventional standards.
- [00122] Referring to FIG. 2, reference numeral 100 generally refers to a coating line incorporating the invention. A metal strip 12 such as annealed cold reduced steel is passed directly from the manufacturing of a strip or is unwound from a coil on an uncoiler by drive rollers. After surface treating, the strip 12 is electrically grounded (e.g., by a metal contact roller), and horizontally passed through an enclosed coater 60 where plastic powder 62 is negatively or positively charged using a voltage of about 5 to about 200 kV, preferably from about 20 to about 90 kV and thereafter deposited onto the top and/or bottom surface of strip 12. It will be understood that strip 12 also could be vertically passed through chamber 60. After being coated with a plastic powder, strip 12 is passed through a hardening device 70 (e.g., convection oven) wherein the powder is at least partially hardened by drying or curing. Optionally, after the flowing and/or curing is completed, the coating may be cooled rapidly to form a tightly adherent coating by passing the coated strip through an air or liquid

quench, such as water. A dryer [not shown] then dries the quenched strip, such as by a pair of air knives for blowing the water from strip 12. Coated strip 10 then may be cut into lengths by a shear or rewound into a coil by a coiler.

- [00123] Coating line 100 optionally may include a pair of opposing presses, a cleaner, or a preheater. After surface pretreatment 50, strip 12 may be preheated *e.g.*, by passing through an induction heater. A preheater is used to heat strip 12 to an elevated temperature when it is desired to apply thick coatings to a metal strip.
- [00124] It is also possible to send a series of metal blanks cut from a continuous coil through coating line 10. In this case, it will be necessary to support the blanks on one side by a conveyor or alternatively suspend the blanks from an overhead conveyor system.
- [00125] It will be understood plastic powders of the invention is meant to include thermoplastic and thermosetting generally having a particle size of from about 0.2 to about 100 microns in diameter. Acceptable thermosetting powders include polyester, epoxy, polyester-epoxy hybrid, acrylic and urethane. It also will be understood coatings formed when using these powders in accordance with the invention generally include thicknesses of at least about 10 microns. Drawn appliance components require coatings having good forming characteristics, excellent surface quality and corrosion resistance, and thicknesses of from about 25 to about 125 microns. Applications such as lockseam formed culvert or transmission pipe requiring thicker coatings of from about 125 to about 250 microns generally need good forming characteristics but not necessarily good cosmetic appearance.
- [00126] It will be understood by strip is meant to include sheet thicknesses of 0.25 mm or more and foil thicknesses of less than 0.25 mm. For sheet thicknesses of about 0.25 mm or more, a low induction frequency of

- 36 -

less than 10 kHz, preferably is used. For foil thicknesses of less than 0.25 mm such as electrical steel or amorphous metals, high frequencies up to 450 kHz may be used. Unlike noninduction heating which generally heats the outer surface of the coating, induction heating heats from the inside out. That is to say, the inner portion of the coating cross section is heated first with the surface portions of the coating being heated last. For steel strip having a thickness of about 0.75 mm or more, a frequency of about 3-6 kHz preferably is used to uniformly heat the entire cross section of the coating. For thermoplastic powder, heater 24 allows the fused coating material to remain molten for sufficient time, *e.g.*, at least 5 seconds, to flow the coating material to even out any thickness nonuniformity and have a smooth surface. If thermosetting powder is used, heater 24 has the additional function of holding the fused coating for sufficient time, *e.g.* at least 15 seconds, above the curing temperature to substantially complete the curing to form a ductile coating so that the coated strip can be fabricated without cracking the coating.

- [00127] In one embodiment, there is disposition of upper spray guns and lower spray guns. Coating chamber 60 is generally enclosed by a wall 64 and includes a chamber bottom 66 (FIG. 3), a strip entrance 67, and a strip exit 68. Coating chamber 60 can also include a gas recirculating system (not shown) for collecting powder which does not become attached to strip 12. In another embodiment, the coating chamber 60 is maintained at a reduced pressure so that powder collected in bottom can be recycled back to the pumps supplying pressurized powder to the spray guns. Powder not attracted to strip 12 may build up on any surface inside chamber 60, such as endwall ledges, support members, and particularly the spray guns. Periodically, this accumulated powder is sloughed off the surfaces and falls within chamber 60. For those surfaces above strip 12, this sloughed powder can fall onto the upper surface of strip 12 resulting in an area of defective coating. For this

reason, the coating system should be designed to exclude any surfaces that can accumulate powder from being within the coating chamber above the passing strip.

- [00128] The reduced pressure within coating chamber 60 from the vacuum of the gas recirculating system for collecting undeposited powder causes sufficient air draft to prevent any undeposited powder from spray guns from escaping to outside of the chamber 60 into the work area.
- [00129] In one embodiment, several spray guns are transversely positioned and evenly spaced across the width of a wide horizontally moving metal strip to insure complete substrate coverage. Because of gravity and the reduced pressure in chamber 60, some of the powder particles blown from lower spray guns may not reach and become attached to bottom surface of strip 12. If so, the thickness of the powder layer deposited by bottom spray guns would be less than the thickness of the powder layer deposited by upper spray guns. To insure the bottom powder thickness is about the same as the top powder thickness, additional more closely spaced spray guns may be installed below the strip. Alternatively, the same number of spray guns can be used below the strip as above the strip if the nozzles of the lower spray guns can be adjusted to increase the powder output. Spray guns are generally spaced so that there is minimal overlap of the powder spray pattern.
- [00130] In some applications it is desirable to produce a thinner coating on one side of the strip than that on the other side of the strip. Such a coating is commonly referred to as a differential coating or a differentially coated strip. For differentially coated strip, the thin coated side could be produced as the top side of a horizontally coated strip. The number of spray guns above the strip could be the same as or fewer than the number of spray guns below the strip. The nozzles of the upper spray guns can be adjusted to reduce the powder flow, as necessary, to obtain the desired reduced coating thickness.

- [00131] The spray guns are generally aligned parallel to the strip rolling direction or passline direction. In one embodiment, the spray guns are positioned pointed toward oncoming strip 12. Charged powder is attracted toward strip 12 by traveling within an electrostatic field established between the spray gun and the metal strip. When the spray guns are near one another, *i.e.*, adjacent to one another, the electrostatic field of one spray gun may intersect that of an adjacent spray gun causing interference in the direction of travel of the charged particles toward strip 12. This interference or repelling of similarly charged particles may cause lines of uneven powder thicknesses along the length of strip 12. Staggering the positions of the spray guns can eliminate this interference.
- [00132] Generally, the content of the antimicrobial metal containing particles in the final coating ranges from about 0.2 to about 30 weight percent based on the final, dried film weight of the coating. This is also on a weight percent based on the weight of the total solids of the applied coating. The content of the antimicrobial particles in the final coating of the present invention is preferably at least about 0.5 weight percent, more preferably at least about 2 weight percent, and most preferably at least about 5 weight percent based on the final, dried film weight of the coating. The content of the antimicrobial particles in the final coating of the present invention is preferably at most about 20 weight percent, more preferably at most about 15 weight percent, and most preferably at most about 10 weight percent based on the final, dried film weight of the coating.
- [00133] When coating a metal substrate with the powder coating composition of the present invention, the coating composition is applied to the metal using any suitable powder coating technique, such as blade coater method, gravure coater method, beat coater method, roll coater method, curtain flow coater method, dip coater method, and spray

coater method, spin coating, brushing, and electro-deposition. The applied coating should cover the area of the metal substrate that is desired to be coated.

- [00134] Preferably, a conventional powder coating apparatus is used as illustrated in FIG. 3. The sheet may be coated in more than one application to the same sheet in order to provide additional thickness to the final coating. Such multiple coatings may have additional washing, drying and curing stages associated with each coating.
- [00135] A common technique for applying a powder coating to an object makes use of electrostatic powder spray coating equipment. In such application, a coating powder is dispersed in an airstream and passed through a high voltage field whereby the coating particles attain an electrostatic charge. These charged particles are attracted to and deposited on the object to be coated that is usually at room temperature. Subsequently, the object is cured, e.g., being placed in an oven and heated whereby the powder melts/cures to form the desired coating on the object. See U.S. Pat. Nos. 5,009,367, 5,027,742, 5,158,986, 5,334,356, 5,207,954, 4,582,731, 4,734,451, 5,290,827, 5,399,597, 5,399,597, incorporated herein by reference in their entirety.
- [00136] Conventionally, the manufacture of a powder coating comprises melt-mixing a resin, a curing agent, plasticizers, stabilizers, flow aids, pigments, and extenders. Whereas dry blending is commonly used to make PVC powders under conditions not amenable to the formation of very fine powders, melt-mixing involves the high speed, high intensity mixing of dry ingredients in a mixer or the like and then the heating of the mixture to an elevated temperature (generally from about 180 to about 250°C.) in a continuous compounder such as a single or twin screw extruder to achieve thorough dispersion of the other ingredients in the resin as the resin melts, forming a molten mixture. The molten

- 40 -

mixture is then cooled to quench the reaction and crushed. Such processing is then generally followed by a sequence of operations which can involve grinding, sifting, separation, and filtering, followed by more sieving.

[00137] In an alternate embodiment, the metal sheet is coated in more than one application using at least two different types of coatings. In one exemplary method, the first application is a paint or polymer coating without antimicrobial oxide, phosphate or zeolite additives. At least the final coating application is a polymer coating containing antimicrobial oxide, phosphate or zeolite additives. The first layer can be used to impart either additional thickness of the total coating, to minimize the total amount of antimicrobial oxide or zeolite additives necessary to coat a given sheet (since only the top surface must have these additives), or to impart other characteristics as known in the art, *e.g.*, additional corrosion resistance coatings, additional or alternative colorants, improved hardness, weather resistance, chemical resistance and other properties.

5. Coat Curing, Drying or Setting

[00138] After a coating composition is applied, the coating is at least partially cured to harden and adhere the coating to the metal sheet. Curing occurs after sufficient melting and flow of the resin to ensure coverage of the strip with a substantially continuous film.

[00139] The curing is by means suitable to the polymer composition used. Curing can be by heating, infrared radiation, fluorescent radiation, ultraviolet radiation, gamma or beta radiation, X-ray radiation, or combinations thereof. In an exemplary method, the sheet, immediately after coating, is passed through a gas-fired heating zone where solvents are evaporated and the resin is cured or dried. Preferably, the polymer is at least partially cured by heat. Heat curing is to raise the

temperature of the coating to accelerate cross-linking reaction. Heat curing can be by various heating means such as an electric heating oven, hot air heating oven, infrared heating oven, and high-frequency heating oven. For curing, a heating temperature and time are properly selected in consideration of the formulation of a coating composition, the size and gage of sheet metal, the capacity of an oven, and other factors. The particular temperature is dependent on such things as the particular epoxy, curing agent and catalyst employed and curing time desired. The temperature, however, should not be so great that the cured coating is degraded, for example, by decomposing. Generally, the drying or curing treatment is carried out under normal pressure or reduced pressure at a temperature of at least about 50°C to at most about 400°C. Preferably the peak metal temperatures (PMT) for the coated metal sheets is at least about 100°C., more preferably at least about 150°C and most preferably at least about 200°C. Preferably the peak metal temperatures (PMT) for the coated metal sheets is at most about 350°C, more preferably at most about 300°C and most preferably at most about 275°C.

[00140]

The time at the temperature of cure can be any practicable time and is desirably as short as practical. Generally, the time at the curing temperature is at least about 0.1 minute to at most about 24 hours. Preferably the time at the cure temperature is at least about 10 minutes, more preferably at least about 5 minutes and most preferably at least about 0.5 minute. Preferably the time at the cure temperature is at most about 2 hours, more preferably at most about 1 hour and most preferably at most about 0.5 hour. As well within the knowledge of those skilled in the art, the temperature and time are in a relative relationship and also the conditions vary depending on the properties of coating required.

- [00141] Immediately after heating to cure or dry the coating, the coated metal sheet may then be subjected to quenching in order to harden the coating prior to the final coiling of the sheet product. The quenching can be by any suitable means as known in the art such as by water or other coolant immersion, spray, or mist or by cold air. The coated metal sheet is then typically coiled by conventional means in metal coils.
- [00142] The thickness of the coating of the present invention is preferably in the range of from about 0.5 to about 30 microns. Preferably thickness of the coating is at least about 2 microns, more preferably at least about 3 microns and most preferably at least about 4 microns. Preferably the thickness of the coating is at most about 20 microns, more preferably at most about 15 microns and most preferably at most about 10 microns.
- [00143] After curing, the applied coating composition, a metal sheet having a cured resin coating adhered thereto is formed generally having antimicrobial properties. Also, the coating that is formed, typically, has improved fingerprint resistance. The coating also protects the surface from staining when tested against kitchen spills such as ketchup, mustard and pickle juice.
- [00144] Generally, a silver-bearing refractory compound is incorporated into a polyester or epoxy film coating to control the growth of harmful bacteria, mold and mildew. These film coatings may be economically applied to stainless or carbon steel products on full size production coils by means of roll coating. The antimicrobial properties may last for years depending on the intended application. Clear or pigmented film coatings can be used.
- [00145] Preferably, silver ions are encapsulated within a zeolite refractory. The zeolite powder is blended into either a polyester or epoxy resin. A thin

- 43 -

film coating, about 0.00025" thick, is applied to either a carbon or stainless steel sheet. The silver ions have great mobility and can diffuse to the surface of the steel to inhibit the growth of bacteria and mold.

[00146] Silver has long been recognized for its safe antimicrobial properties. Coated products may be effective against many common food borne pathogens such as Escherichia coli, Salmonella and Listeria monocytogenes as well as various types of mold including Aspergillus niger.

[00147] On metals, such as stainless steels, the zeolite refractory compound, when added to a clear resin coating, hides fingerprints due to the light scattering influence of the micron-scale diameter zeolite particles contained within the coating matrix. The resin coating also protects the surface from staining when tested against kitchen spills such as ketchup, mustard and pickle juice.

Examples.

Example 1.

[00148] Cold rolled carbon steel with a thickness of 0.028" and a width of 44.00" is run though the powder coating process at a line speed of about 100 to about 200 fpm. The steel strip is cleaned using an alkaline cleaner of potassium hydroxide at about 1 to about 2% concentration, dwell time of about 3 to about 10 seconds, and at a temperature of from about 150 to about 160 °F using about 40 to about 60 psi spray. The steel strip is then rinsed with a water rinse for about 2 to about 4 seconds at about 100 °F.

[00149] The steel strip is then pre-treated with a chemical conditioning rinse of iron phosphate compound (BONDERITE 902 from Henckel, Inc.) for a time about 5 to about 10 seconds, with about 150 to about 250 mg/sq ft coating weight, at a temperature of about 140 to about 150 °F. The

- 44 -

strip is then rinsed with a clear water rinse for about 2 to about 4 seconds at about 100 °F.

- [00150] The steel strip is then treated with a chrome rinse post-treatment of Parcolene 62 applied at a concentration of 2% in water, composed of chromic acid, hydrofluoric acid and zinc chromate, for an exposure time of about 2 to about 5 seconds, at a pH of about 3.2 to about 3.7, at a temperature of about 120 °F.
- [00151] By means of a powder coater, the strip is then coated with a white colored ALFA WHITE APPLIANCE POWDER polyester (Dupont, Inc. USA) containing of about 1 to about 3 wt.% based on dried coating of an antimicrobial powder (AgION Technologies, Inc., AJ10D, an AgION white powder - Zeolite crystal structure, has a particle size of about 2.5 mm, about 2.5% silver, about 14% zinc, a pH of about 9 and about 2% water.). The coating is applied by means of an electrostatic powder coating system.
- [00152] The metal sheet is cured in a first induction oven to a Peak Metal Temperature of about 250 to about 300 °F, and then in a second induction oven to a Peak Metal Temperature of about 450 to about 500 °F, then water quenched to a metal temperature of less than about 150°F, producing a white, polyester coating, with about 7 Wt-% silver zeolite, based on dried coating, with a coating thickness of from about 1.4 to about 1.8 mils, dry film thickness.
- [00153] Adhesion as measured with 2T bend-test is excellent, showing no paint removal. MEK rubs are about 100+ and Pencil Hardness is about 3H. Subsequent efficacy tests conducted using *E. coli* bacteria indicate about a 99.99% reduction in bacteria. Fingerprint resistance is excellent.

Example 2.

- 45 -

- [00154] Cold rolled carbon steel with a thickness of 0.028" and a width of 46" is run through the powder coating process at a line speed of about 100 to about 200 fpm. The steel strip is cleaned using an alkaline cleaner of potassium hydroxide at about 1 to about 2% concentration, dwell time of about 3 to about 10 seconds, and at a temperature of from about 150 to about 160 °F using about 40 to about 60 psi spray. The steel strip is then rinsed with a water rinse for about 2 to about 4 seconds at about 100 °F.
- [00155] The steel strip is then pre-treated with a chemical conditioning rinse of iron phosphate compound (BONDERITE 902 from Henckel, Inc.) for a time about 5 to about 10 seconds, with about 150 to about 250 mg/sq ft coating weight, at a temperature of about 140 to about 150 °F. The strip is then rinsed with a clear water rinse for about 2 to about 4 seconds at about 100 °F.
- [00156] The steel strip is then treated with a chrome rinse post-treatment of Parcolene 62 applied at a concentration of 2% in water, composed of chromic acid, hydrofluoric acid and zinc chromate, for an exposure time of about 2 to about 5 seconds, at a pH of about 3.2 to about 3.7, at a temperature of about 120 °F.
- [00157] By means of a powder coater, the strip is then coated with a white colored ALFA WHITE APPLIANCE POWDER polyester (Dupont, Inc. USA) containing of about 1 to about 3 wt.% based on dried coating of an antimicrobial powder (AgION Technologies, Inc., AJ10D, an AgION white powder - Zeolite crystal structure, has a particle size of about 2.5 mm, about 2.5% silver, about 14% zinc, a pH of about 9 and about 2% water.). The coating is applied by means of a powder coating system.
- [00158] The metal sheet is cured in a first induction oven to a Peak Metal Temperature of about 280 °F, and then in a second induction oven to a

- 46 -

Peak Metal Temperature of about 480 °F, is then water quenched to a metal temperature of less than about 150°F, producing a white, polyester coating, with about 7 Wt-% silver zeolite, based on dried coating, with a coating thickness of from about 2.5 to about 3.5 mils, dry film thickness.

- [00159] Adhesion as measured with 2T bend-test is excellent, showing no paint removal. MEK rubs were about 100+ and Pencil Hardness is about 6H. Efficacy test results are similar to those reported in Example 1. Fingerprint resistance is excellent.

Example 3.

- [00160] Same as above with the following parameters:
- [00161] Cold rolled carbon steel with a thickness of 0.028" and a width of 39" is run though the powder coating process at a line speed of about 100 fpm. The steel strip is cleaned using an alkaline cleaner of potassium hydroxide at about 1 to about 2% concentration, dwell time of about 3 to about 10 seconds, and at a temperature of from about 150 to about 160 °F using about 40 to about 60 psi spray. The steel strip is then rinsed with a water rinse for about 2 to about 4 seconds at about 100 °F.
- [00162] The steel strip is then pre-treated with a chemical conditioning rinse (NUPAL 150B from PPG, Inc). The strip is then rinsed with a clear water rinse.
- [00163] By means of a powder coater, the strip is then coated with a blue tinted epoxy powder coating (Dupont, Inc. USA) containing of about 1 to about 3 wt.% based on dried coating of an antimicrobial powder (AgION Technologies, Inc., AJ10D, an AgION white powder - Zeolite crystal structure, has a particle size of about 2.5 mm, about 2.5% silver, about 14% zinc, a pH of about 9 and about 2% water.). The coating is applied by means of a powder coating system.

- 47 -

- [00164] The metal sheet is cured in a first induction oven to a Peak Metal Temperature of about 220 °F, and then in a second induction oven to a Peak Metal Temperature of about 420 °F, then water quenched to a metal temperature of less than about 150°F, producing a blue tinted, polyester coating, with about 7 Wt-% silver zeolite, based on dried coating, with a coating thickness of from about 2.0 to about 3.0 mils, dry film thickness.
- [00165] Adhesion as measured with 2T bend-test is excellent, showing no paint removal. MEK rubs are about 100+ and Pencil Hardness is about 5H. Efficacy results are similar to Example 1. Fingerprint resistance is excellent.

Claims

1. A process of manufacturing a metal sheet precoated with an antimicrobial polymer coating, comprising:

providing a metal sheet substrate having two opposed planar surfaces comprising a base metal selected from the group consisting of aluminum, iron, nickel, titanium, molybdenum, magnesium, manganese, copper, silver, lead, tin, chromium, beryllium, tungsten, cobalt and alloys thereof;

applying a polymer coating onto at least one planar surface of the substrate by powder coating the substrate with a polymer containing an antimicrobial powder comprising core particles associated with an antimicrobial metal component;

10 wherein the core particle is an oxide selected from the group consisting of titanium, aluminum, zinc and copper, sulfates of calcium, strontium and barium, zinc sulfide, copper sulfide, zeolites, zirconium phosphate, mica, talc, kaolin, mullite, silica and mixtures thereof;

15 wherein the antimicrobial metal component is selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions and mixtures thereof; and

treating the coated substrate to produce at least a partially hardened and adhered antimicrobial coating on the final sheet product.

2. The process of claim 1 wherein the base metal is a metal selected from the group consisting of steel, nickel, zinc, iron, aluminum, copper and mixtures thereof.
3. The process of claim 2 wherein the metal sheet is provided as a continuous strip.
4. The process of claim 3 additionally comprising the step of cleaning the surface of the substrate wherein cleaning comprises removing bulk and molecular organic contaminants prior to applying a polymer coating.

5. The process of claim 4 wherein the cleaning step comprises one or more
cleaning methods selected from the group consisting of solvent cleaning,
emulsion cleaning, alkaline cleaning, acid cleaning, pickling, salt bath
descaling ultrasonic cleaning, and combinations thereof.
10. The process of claim 4 additionally comprising the step of pretreating at least
one planar surface of the substrate to promote adhesion of a polymer coating
prior to applying a polymer coating.
15. The process of claim 6 wherein the pretreating creates a chemical conversion
interlayer coating selected from the group consisting of a silane, phosphate,
chromate, epoxy, oxide, adhesive and mixtures thereof.
20. The process of claim 4 wherein the polymer is an organic polymer material
selected from the group consisting of acetate rayon, acrylic resins,
acrylonitrile-butadiene-styrene resins and acrylic resins, aliphatic and aromatic
polyamides, aliphatic and aromatic polyesters, allyl resins, butadiene resins,
chlorinated polyethylene, conductive resins, copolymerised polyamides,
copolymers of ethylene and vinyl acetate, cuprammonium rayons and natural
and synthetic rubbers, EEA resins, epoxy resins, ether ketone resins, ethylene
vinyl alcohol, fluorine resins, fluotocarbon polymers, fluoroplastics, high
density polyethylenes, ionomer resins, liquid crystal polymer, low density
polyethylenes, melamine formaldehyde, natural polymers such as cellulosics,
nylons, phenol-formaldehyde plastic, phenolic resins, polyacetal,
polyacrylates, polyacrylonitrile, polyamide, polyamide-imide,
polyaryletherketone, polybutadiene, polybutylene terephthalate, polybutylene,
polycarbonate, polycarbonates, polydicyclopentadiene, polyketones, polyester
block copolymers, polyesters, polyesterurethane, polyesterurethaneurea,
polyether and polyester block polymers, polyether ketoneketone
polyetherether ketone polyetherimide, polyethers, polyethersulfone,
polyetherurethane, polyetherurethaneurea, polyethylene isophthalate,
polyethylene terephthalate, polyethylene, polyethylenechlorinates,
polyglycolic acid, polyhexamethylene terephthalate, polyimide, polylactic

- 50 -

- acid, polymethylpentene, poly-m-phenylene isophthalamide, polyolefins, polyphenylene oxide, polyphenylene sulfide, polyphthalamide, poly-p-phenylene terephthalamide, polypropylene, polysiloxanes, polystyrene, polysulfides, polysulfone, polytetrafluoroethylene, polyurethane, polyvinyl acetate, polyvinyl alcohols, polyvinylchloride, polyvinylidene chloride, polyvinylidene fluoride and polyvinyl fluoride, rayon, reconstituted silk and polysaccharides, reinforced polyethylene terephthalate resins, segmented polyurethane elastomers, silicone resins, elastane elastomers, styrene-type specific resins, thermoplastic polyurethane elastomers, phenol-formaldehyde copolymer, triacetate rayon, unsaturated polyester resins, urea resins, urethane resins, vinyl chloride resins, vinyl polymers, vinylidene chloride resins and copolymers, terpolymers and mixtures thereof.
9. The process of claim 4 wherein the polymer is a thermosetting composition comprising a resin composition, wherein the resin is selected from the group consisting of a polyester resin, an acrylic resin, a nylon resin, a fluororesin resin, and an epoxy resin
- 5 10. The process of claim 4 wherein the polymer is an epoxy selected from the group consisting of phenolic-modified epoxies, polyester-modified epoxies, epoxy-modified polyvinyl chloride, and cross-linkable epoxies.
11. The process of claim 10 wherein the epoxy has at least one reaction group selected from the group consisting of hydroxyl, acid and epoxy groups.
- 10 12. The process of claim 8 wherein the polymer further comprises at least one additional component selected from the group consisting of defoamers, crosslinkers, catalysts, stabilizers, delustering agents, whitening agents, pigments, fillers, plasticisers, ultraviolet absorbers, antioxidants, light stabilizers, ultraviolet stabilizers, processing stabilizers, and metal deactivators.
- 15 13. The process of claim 8 wherein the powder coating is applied by the method selected from the group consisting of electrostatic, triboelectric,

- 51 -

20 electromagnetic brush, fluidized bed, plasma physical vapor deposition, electrostatic fluidized bed, thermal fluidized bed, knife coating, gravity feed and water suspended powder spray methods.

14. The process of claim 13 wherein the polymer is applied by two or more coaters placed in series.
15. The process of claim 13 wherein the polymer coating is at least partially hardened by a method selected from the group consisting of heat, infrared radiation, fluorescent radiation, ultraviolet radiation, gamma or beta radiation, X-ray radiation, or combinations thereof.
16. The process of claim 13 wherein the core particle is a natural zeolite selected from the group consisting of analcime, chabazite, clinoptilolite, erionite, faujasite, mordenite, and phillipsite.
17. The process of claim 13 wherein the core particle is a synthetic zeolite selected from the group consisting of A-type zeolite, X-type zeolite, Y-type zeolite, and mordenite.
18. The process of claim 17 wherein the synthetic zeolite comprises ion-exchangeable ions partially or completely ion-exchanged with antibiotic metal ions.
19. The process of claim 18 wherein the ion-exchangeable ions are selected from the group consisting of sodium ions, potassium ions, calcium ions, magnesium ions and iron ions and wherein the antibacterial metals ions are selected from the group consisting of silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, and thallium ions or mixtures thereof, and wherein the zeolite particles retain the antibacterial metal ions at ionic exchange sites of the zeolite in an amount less than the ion exchange saturation capacity of the zeolite.
5

- 52 -

20. The process of claim 19 wherein the zeolite is ion-exchanged with metal ions in an amount less than about 90% of the ion-exchangeable saturation capacity of the zeolite particles.
21. The process of claim 20 wherein the antibacterial metals ions are selected from the group consisting of silver, copper or zinc ions or mixtures thereof.
22. The process of claim 21 wherein additional metal ions selected from the group consisting of sodium, potassium, magnesium, calcium, aluminum, titanium, cerium and ammonium ion co-exist on the zeolite.
23. The process of 21 wherein the amount of antimicrobial component on the core particle is at least about 0.1% by weight.
24. The process of claim 18 wherein the antimicrobial powder has a second coating of a composition selected from the group consisting of silica, silicates, silicon dioxide, borosilicates, aluminosilicates, alumina, aluminum phosphate, zinc, zinc oxide, zinc silicate, copper, copper oxide, and mixtures thereof.
25. The process of claim 18 wherein the antimicrobial powder is additionally coated with a dispersion enhancing coating selected from the group consisting of resin, hydrous metal oxide, and mixtures thereof.
26. A metal sheet precoated with an antimicrobial polymer coating manufactured by the method of claim 8.
27. A process of increasing stain resistance of a metal sheet by the method of claim 8.
- 5 28. A process of increasing fingerprint resistance of a metal sheet by the method of claim 8.
29. A process of decreasing the gloss value of a metal sheet by the method of claim 8.

- 53 -

30. The process of claim 29, wherein the powder coating composition forms a
10 coating having a gloss value measured at a 60° angle of about 0.7% to about
45%.

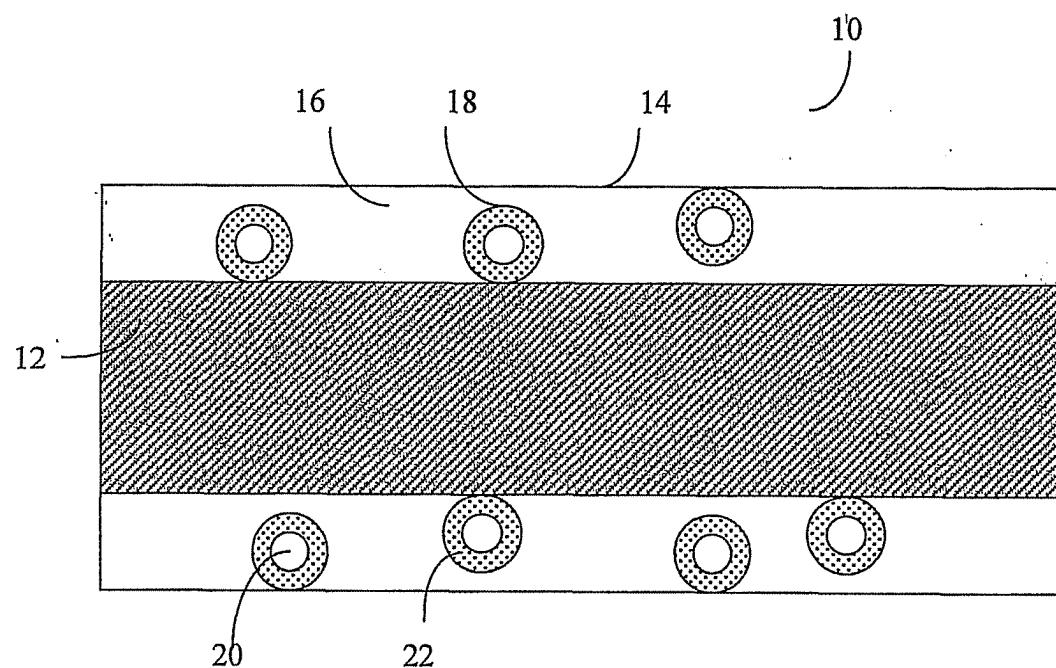


FIG. 1.

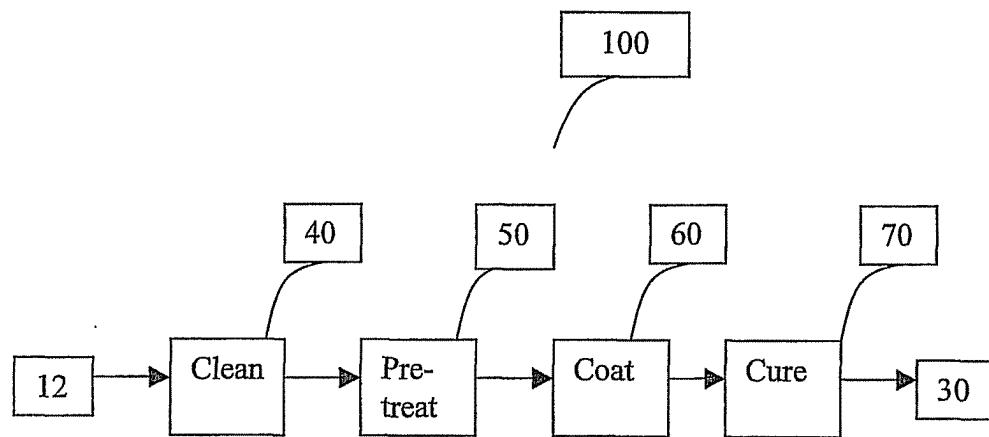


FIG. 2.

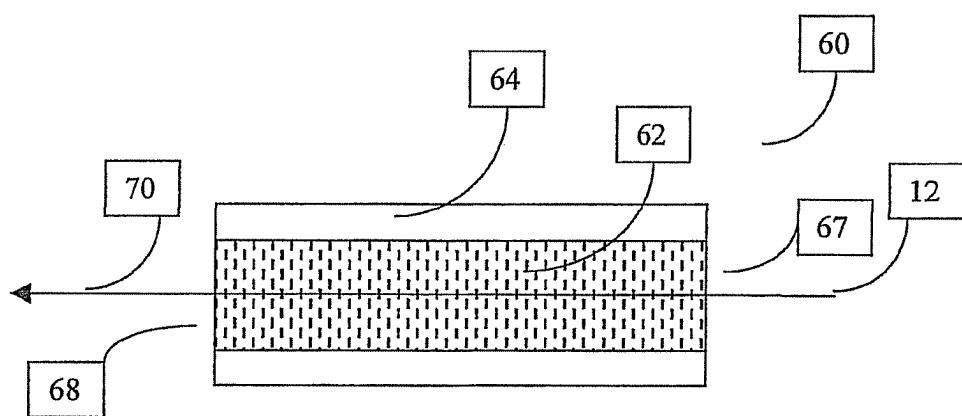


FIG. 3.

INTERNATIONAL SEARCH REPORT

PCT/US 02/13637

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N59/16 A01N25/34 C09D5/14 B05D7/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N C09D B05D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 093 407 A (GOTTSCHLING PETER ET AL) 25 July 2000 (2000-07-25) the whole document	1-30
E	-& US 6 432 416 B1 (GOTTSCHLICH PETER ET AL) 13 August 2002 (2002-08-13) column 2, line 57 -column 3, line 12; claims; examples 5,6 —	1-30
Y	US 5 180 585 A (JACOBSON HOWARD W ET AL) 19 January 1993 (1993-01-19) cited in the application column 1, line 25 -column 3, line 7 column 8, line 40 -column 9, line 36 column 10, line 6 - line 28 column 10, line 43 - line 59 column 11, line 38 -column 12, line 16; claims 1-8,14 — —/—	1-30

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

20 September 2002

07/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Muellners, W

INTERNATIONAL SEARCH REPORT

PCT/US 02/13637

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199708 Derwent Publications Ltd., London, GB; Class D22, AN 1997-083611 XP002214144 & JP 08 325482 A (NIPPON PAINT CO LTD), 10 December 1996 (1996-12-10) abstract ----	1-30
X	DATABASE WPI Section Ch, Week 199750 Derwent Publications Ltd., London, GB; Class A82, AN 1997-545618 XP002214215 & JP 09 263715 A (TOMOEGAWA SEISHISHO KK), 7 October 1997 (1997-10-07) abstract ----	1-30
A	DATABASE WPI Section Ch, Week 198947 Derwent Publications Ltd., London, GB; Class A82, AN 1989-343325 XP002214145 & JP 01 254782 A (NIPPON PAINT CO LTD), 11 October 1989 (1989-10-11) abstract ----	1,26-30
A	US 5 491 202 A (UMEHARA TAKAFUMI ET AL) 13 February 1996 (1996-02-13) column 1, line 16 - line 25; tables 3,4 ----	1,26-30
A	US 5 387 473 A (YOSHIMI NAOTO ET AL) 7 February 1995 (1995-02-07) column 1, line 6 - line 27 column 5, line 4-21 column 9, line 65 -column 10, line 20 column 16, line 8 - line 48 column 19, line 56 -column 20, line 2; claims 1,5 ----	1,27-30
A	US 5 681 890 A (NAKANO TAKASHI ET AL) 28 October 1997 (1997-10-28) column 1, line 6 - line 35; claim 1 ----	1,27
A	LEACH R C: "The Preparation, Powder Coating, and Curing of Precut Metal Sheets for Postforming" METAL FINISHING, ELSEVIER SCIENCE PUBLISHING, NEW YORK, NY, US, vol. 93, no. 4, 1 April 1995 (1995-04-01), pages 24,26-27, XP004024617 ISSN: 0026-0576 page 24 page 26 ----	1,26
	-/-	

INTERNATIONAL SEARCH REPORT

PCT/US 02/13637

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 02 40180 A (KRAKOVICH RICHARD L ;SSW HOLDING COMPANY INC (US)) 23 May 2002 (2002-05-23) page 1, line 12 - line 15 page 2, line 23 -page 3, line 5 page 6, line 10 - line 28 page 9, line 1 - line 17 page 9, line 27 - line 29; claims 1,5 _____	1-30

INTERNATIONAL SEARCH REPORT

PCT/US 02/13637

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 6093407	A	25-07-2000	US	6432416 B1	13-08-2002
			AU	9542298 A	27-04-1999
			BR	9812847 A	08-08-2000
			CA	2305347 A1	15-04-1999
			CN	1280599 T	17-01-2001
			WO	9918162 A1	15-04-1999
			EP	1034224 A1	13-09-2000
			NO	20001685 A	23-05-2000
US 5180585	A	19-01-1993	WO	9415462 A1	21-07-1994
			AU	3441293 A	15-08-1994
			DE	69321139 D1	22-10-1998
			DE	69321139 T2	12-05-1999
			EP	0677989 A1	25-10-1995
			JP	8505858 T	25-06-1996
			US	5503840 A	02-04-1996
			US	5643592 A	01-07-1997
			US	5595750 A	21-01-1997
JP 8325482	A	10-12-1996	NONE		
JP 9263715	A	07-10-1997	NONE		
JP 1254782	A	11-10-1989	NONE		
US 5491202	A	13-02-1996	JP	3211469 B2	25-09-2001
			JP	6293867 A	21-10-1994
US 5387473	A	07-02-1995	JP	5331657 A	14-12-1993
			DE	4310316 A1	02-12-1993
			KR	9613479 B1	05-10-1996
US 5681890	A	28-10-1997	JP	8245905 A	24-09-1996
			JP	8245906 A	24-09-1996
			KR	185679 B1	01-04-1999
WO 0240180	A	23-05-2002	AU	2578002 A	27-05-2002
			WO	0240180 A1	23-05-2002